Claims

We claim:

1. A method of fragmenting ions, comprising:

trapping ions in a an ion trap, the trap being disposed in or providing an environment in which a neutral background gas is present at a pressure of less than approximately 9×10^{-5} Torr;

resonantly exciting selected trapped ions by subjecting them to an alternating potential to thereby promote collision-induced dissociation of at least a portion of the trapped ions; and

dampening the oscillatory motion of the resonantly excited selected ions approaching a periphery of the trap to thereby reduce the probability of the selected ions ejecting from the trap.

2. A method according to claim 1, wherein the pressure is in the range of approximately 1×10^{-5} Torr and approximately 9×10^{-5} Torr.

3. A method according to claim 1, wherein the excitation period is in the range of approximately 25 ms to approximately 2000 ms.

4. A method according to claim 3, wherein the excitation periods is in the range of approximately 50 ms to approximately 550 ms.

5. A method according to claim 1, wherein the selected trapped ions are subjected to a maximum of a one $\text{Volt}_{(0\text{-pk})}$ alternating potential.

6. A method according to claim 5, wherein the selected trapped ions are subjected to a maximum of 550 $\text{mV}_{(0\text{-pk})}$ alternating potential.

7. A method according to claim 1, wherein the alternating potential has a frequency component substantially equal to a fundamental resonant frequency of a selected ion relative to a trapping field.

8. A method of fragmenting ions, comprising:

trapping ions in a linear ion trap by subjecting the ions to a substantially quadrupolar RF potential, the trap being disposed in an environment in which a background gas is present at a pressure of less than approximately 9×10^{-5} Torr;

resonantly exciting trapped ions of a selected m/z value or values by applying to at least one set of poles straddling the trapped ions an auxiliary alternating excitation signal for a period exceeding approximately 25 milliseconds, to thereby promote collision-induced dissociation of the selected ions; and

dampening the oscillatory motion of the resonantly excited selected ions approaching a radial periphery of the trap to thereby reduce the probability of radially ejecting the selected ions from the trap.

9. A method according to claim 8, wherein the dampening is effected by introducing additional electrodes between electrodes used to produce the quadrupolar RF potential.

10. A method according to claim 9, wherein the linear ion trap comprises a series of poles, and a DC voltage potential exists between the additional electrodes and the poles of the trap.

11. A method according to claim 10, wherein said DC voltage potential is varied depending on the m/z value of the selected ion.

12. A method according to claim 9, wherein the selected trapped ions are subjected to a maximum of one $\text{Volt}_{(0\text{-pk})}$ auxiliary alternating potential.

13. A method according to claim 12, wherein the selected trapped ions are subjected to a maximum of a 550 $\text{mV}_{(0\text{-pk})}$ auxiliary alternating potential.

14. A method according to claim 9, wherein the excitation signal has a frequency substantially equal to a fundamental resonant frequency of the selected ions relative to the quadrupolar field or a harmonic thereof.

15. A method according to claim 9, including mass analyzing the fragmented ions to obtain a mass spectrum.

16. A method of mass analyzing a stream of ions, the method comprising:

(a) subjecting a stream of ions to a first mass filter step, to select precursor ions having a mass-to-charge ratio in a first desired range;

(b) trapping the precursor ions in a linear ion trap, the trap having a substantially quadrupolar RF trapping field superimposed with a higher order multipole field;

(c) resonantly exciting selected trapped precursor ions in the quadrupolar field by subjecting the selected ions to an auxiliary alternating potential having a for an excitation period exceeding approximately 25 milliseconds under a background gas pressure of less than 9×10^{-5} Torr, to thereby generate fragment ions; and

(d) mass analyzing the trapped ions to generate a mass spectrum.

17. A method according to claim 16, wherein the higher order field provides a relatively small contribution to the overall potential near a central longitudinal axis of the linear ion trap.

18. A method according to claim 17, wherein the selected trapped ions are subjected to a maximum of a $1V_{(0\text{-}pk)}$ auxiliary alternating potential.

19. The method according to claim 18, wherein the selected trapped ions are subjected to a maximum of $550\ mV_{(0\text{-}pk)}$ auxiliary alternating potential.

20. A method according to claim 17, including, before step (d):

subjecting the trapped ions to a second mass filter step in order to isolate ions having an m/z value(s) in a second desired range, and

repeating step (c).

21. A method of mass analyzing a stream of ions, the method comprising:

(a) subjecting a stream of ions to a first mass filter step, to select precursor ions having a mass-to-charge ratio in a first desired range;

(b) fragmenting the precursor ions in a collision cell, to thereby produce a first generation of fragment ions;

(c) trapping any un-dissociated precursor ions and the first generation of fragment ions in a linear ion trap in which ions are trapped by a substantially quadrupolar RF field superimposed with a higher order multipole field, and:

(i) subjecting the trapped ions to a second mass filter step, to thereby isolate ions having an m/z value(s) in a second desired range,

(ii) resonantly exciting selected first generation ions in the quadrupolar field by subjecting the selected ions to an auxiliary alternating potential for an excitation period exceeding approximately 25 milliseconds under a background gas pressure of less than 9×10^{-5} Torr, to thereby generate a second generation of fragment ions, and

(d) mass analyzing the trapped ions to generate a mass spectrum.

22. A method according to claim 21, wherein the higher order field provides a relatively small contribution to the overall potential near a central longitudinal axis of the linear ion trap.

23. A method according to claim 22, wherein the selected trapped ions are subjected to a maximum of 1 $V_{(0\text{-pk})}$ auxiliary alternating potential.

24. A method according to claim 23, where the excitation period is in range of approximately 50 ms to approximately 2000 ms.

25. A method according to claim 24, wherein the selected trapped ions are subjected to a maximum of a 550 $mV_{(0\text{-pk})}$ auxiliary alternating potential.

26. A method according to claim 25, wherein the excitation period is in the range of approximately 50 to 550 ms.

27. A method according to claim 21, including repeating steps (c)(i) and (c)(ii) to thereby generate subsequent generations of fragment ions.

28. A method of mass analyzing a stream of ions, the method comprising:

(a) subjecting a stream of ions to a first mass filter step, to select precursor ions having a mass-to-charge ratio in a first desired range;

(b) fragmenting the precursor ions in a collision cell, to thereby produce a first generation of fragment ions;

(c) trapping any un-dissociated precursor ions and the first generation of fragment ions in a linear ion trap in which ions are trapped by a substantially quadrupolar RF field superimposed with a higher order multipole field, and:

(i) subjecting the trapped ions to a second mass filter step, to thereby isolate ions having an m/z value(s) in a second desired range,

(ii) resonantly exciting trapped ions of a selected m/z value or values in the quadrupolar field by applying to at least one set of poles straddling the trapped ions an alternating excitation signal having an amplitude of less than approximately 1 $V_{(0\text{-}pk)}$ for a period exceeding approximately 25 milliseconds, to thereby promote collision-induced dissociation of the selected ions, and

(d) mass analyzing the trapped ions to generate a mass spectrum.

29. A method according to claim 28, wherein the higher order field provides a relatively small contribution to the overall potential near a central longitudinal axis of the linear ion trap.

30. A mass spectrometer, comprising:

a linear ion trap having a quadrupolar rod set for generating a substantially quadrupole RF trapping field and a set of additional electrodes for superimposing a higher order multipole field to the trapping field;

means for providing a background gas in said trap at a pressure of less than approximately 9×10^{-5} Torr;

means for introducing ions into said trap;

means for applying a resonant excitation signal in order to promote collision-induced dissociation of selected ions; and

means for mass analyzing the trapped ions to generate a mass spectrum.

31. A mass spectrometer according to claim 30, wherein a DC voltage potential is present between the rods of the quadrupole rod set and the additional electrodes.

32. A mass spectrometer according to claim 31, wherein said DC voltage potential is varied depending on the m/z value or values of selected resonantly excited ions.

33. A mass spectrometer according to claim 30, wherein selected trapped ions are subjected to an alternating potential from said excitation signal that does not exceed approximately $1V_{(0\text{-pk})}$, for a period exceeding 25 ms.

34. A mass spectrometer according to claim 33, wherein the selected trapped ions are subjected to an alternating potential having a maximum amplitude of 550 $mV_{(0\text{-pk})}$, for a period of less than 550 ms.

35. A mass spectrometer according to claim 30, wherein four additional electrodes are interposed between the rods of the quadrupole rod set in order to approximate an octopole field.

36. A mass spectrometer according to claim 31, wherein each additional electrode is a T-shaped electrode having either a tapering or non-tapering stem section.

37. A mass spectrometer, comprising:

a linear ion trap including means for generating a substantially quadrupole RF trapping field and means for superimposing a higher order multipole field to the trapping field;

means for providing a background gas in said trap at a pressure of less than approximately 9×10^{-5} Torr;

means for introducing ions into said trap;

means for applying a resonant excitation signal in order to promote collision-induced dissociation of selected ions; and

means for mass analyzing the trapped ions to generate a mass spectrum.

38. A mass spectrometer according to claim 37, wherein selected ions trapped in said trap are subjected to an alternating potential from said excitation signal that does not exceed approximately $1V_{(0\text{-}pk)}$, for a period exceeding approximately 25 ms.

39. In a Penning trap having at least four planar or curved-surface electrodes for constraining ions radially and at least two electrodes for constraining ions axially, an improvement comprising at least one additional electrode interposed between any two adjacent radially-constraining electrodes, and a voltage generator for establishing a DC potential voltage between each additional electrode and the adjacent radial-constraining electrode.